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The Dissociation Constant of Hexaphenylethane - A New Spectrophotometric Determination

Technical Report No. 8

to the

OFFICE OF NAVAL RESEARCH

under Project No. NR-055-095

at Harvard University

Contract No. N5ori-76 Task XX

By Paul D. Bartlett and John H. Ridd

Date of Report: 1 September 1952

Period covered: 1 September 1951 - 31 August 1952

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SUMMARY AND INTRODUCTION

Doubts have been cast recently upon the method of applying the diamagnetic correction in estimating the concentrations of long-lived free radicals from measurements of magnetic susceptibility. Only an independent measurement of the degree of dissociation of hexaphenylethane in benzene can decide whether the diamagnetic susceptibility of the radical shows a positive exaltation, as suggested by Selwood and Dobres's experimental work,[20] or a negative one, as suggested by Pullman and Berthier[21] on theoretical grounds.

The very careful determination by Ziegler and Ewald,[17] in 1929 of the dissociation constant of hexaphenylethane by the optical method yielded a value more than twice the average of the later magnetic determinations by Müller,[19] Marvel,[18] and Selwood.[14] In the present work a new optical determination has been made, with efforts to achieve the greatest possible control of purity and reliability of analysis, and to minimize the systematic dilution error by making up every third dilution in a nitrogen box from which the air is removed by evacuation. Despite all efforts, the purity and stability of the material have left something to be desired. The new determination yields a dissociation constant at 20° of 2.0×10^{-4}, which is indistinguishable from those obtained by the magnetic method with the assumption that Pascal's Law applies to the diamagnetic susceptibility of the free radical.

The difficulties attending the preparation of analytically pure hexaarylethanes have appeared in this work to be greater and more varied than the literature suggests. In view of this fact it does not seem wise to pursue our original objective of highly accurate determinations of ΔH and ΔS for the dissociation of series of alkyl-substituted hexaarylethanes.

Preparation and Purification of the Ethane

Hexaphenylethane was prepared by the action of mercury on a solution of triphenylmethyl chloride in toluene. The reaction was carried out in the complete absence of air, using the apparatus shown in Fig. 1. This reaction is one of those originally used by Gomberg[2] in 1900.

The vacuum line consisted of a manifold to which was attached the reaction vessel, a calibrated tube, and a toluene reservoir. This system could be evacuated by a Cenco "Pressovac" pump, or, more completely, by a mercury vapor pump backed by a Cenco "Hyvac." The reaction vessel, comprising the reaction flask A and the receiving tube C, was sealed to the vacuum line, evacuated, flamed out, and tested for leaks. It was then detached and triphenylmethyl chloride (5 g.) was placed in the flask A, together with a small magnetic stirring rod enclosed in glass. Mercury (16 ml.) was introduced into the side-arm B. The reaction vessel was then resealed to the vacuum line and evacuated by the Pressovac pump. The toluene, which had been stored over calcium hydride in Flask E, was then cooled by a carbon dioxide freezing mixture and degassed by opening tap T_1. After about fifteen minutes, when the initially vigorous evolution of gas had ceased, tap T_3 was closed and about 40 ml. of the toluene was condensed in the calibrated cylinder F.

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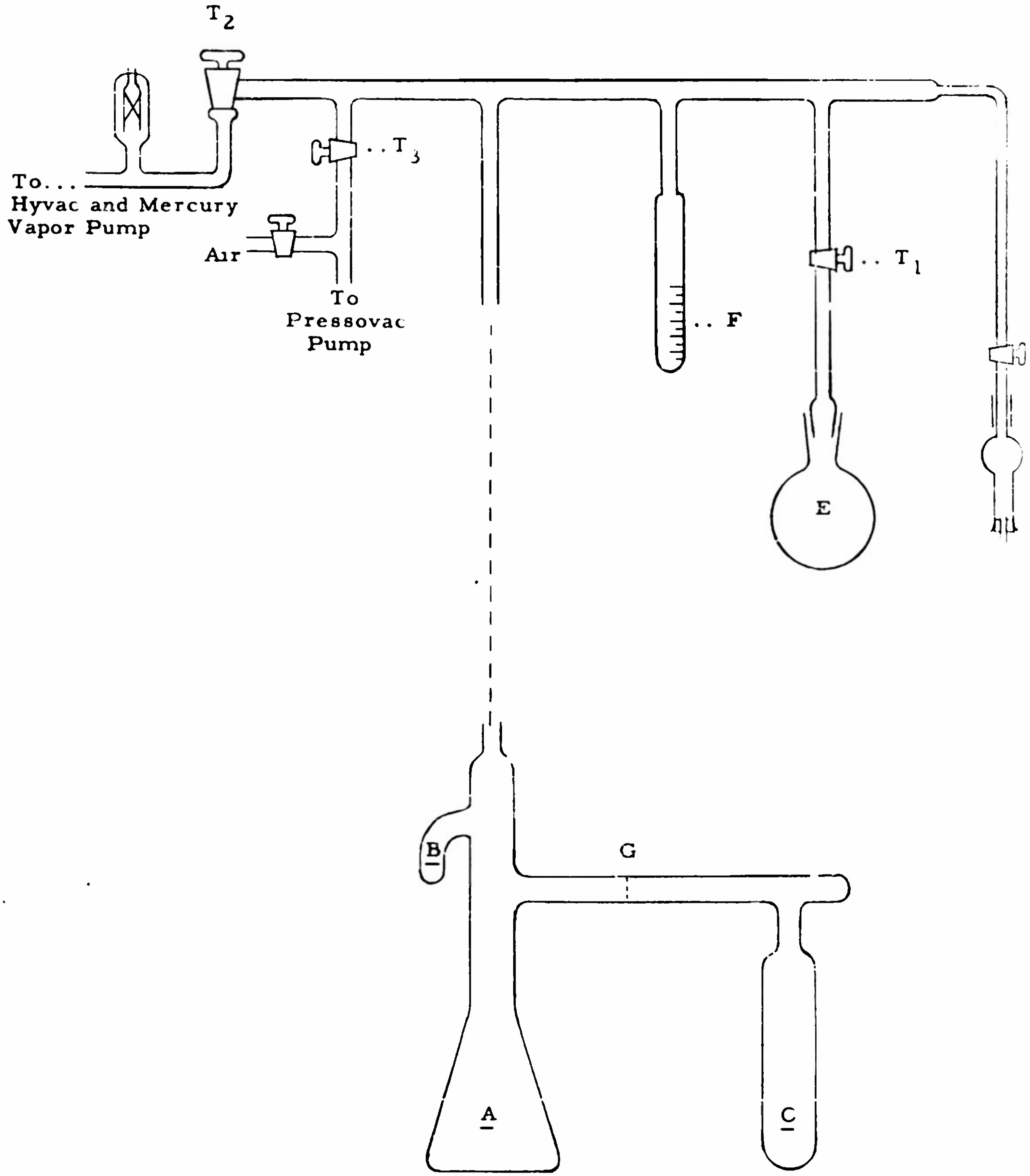
[2] J. Am. Chem. Soc., 22, 757 (1900).

FIG. 1

THE VACUUM LINE AND THE REACTION VESSEL


T_2
To...
Hyvac and Mercury
Vapor Pump
T_3
Air
To
Pressovac
Pump
F
T_1
E
B
G
A
C

THE REACTION VESSEL (LARGER SCALE

Tap T_1 was then closed and this toluene was transferred to the reaction vessel by cooling the latter to -70° C. The vacuum line was then thoroughly pumped out using the mercury vapor and "Hyvac" pump, and the reaction vessel was sealed off under vacuum.

The mercury was transferred to the reaction flask A and the mixture was stirred magnetically for 20 hours in the absence of light. The toluene solution of the ethane was filtered through the sintered glass disc G into the receiving tube C and from this the pure solvent was distilled back by cooling flask A to -70° C. Care was taken to obtain slow crystallization of the ethane and to prevent the rapid solidification of a supersaturated solution. When this happened, about half the pure solvent was returned to the receiving tube and the recrystallization repeated. Removal of the solvent normally required about ten hours, and the receiving tube containing the ethane was then sealed off from the reaction vessel.

Hexaphenylethane, so prepared, forms a 1:1 molecular compound with toluene,[3] and is also contaminated with triphenylmethyl chloride.

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(3) Gomberg and Cone, Ber., 37, 2033 (1904).

It was therefore recrystallized from acetone; this being one of the few solvents that do not form complexes with the ethane.[4] The

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(4) Gomberg, J. Am. Chem. Soc., 24, 597 (1902).

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recrystallization also removed a small quantity of a yellow impurity. The apparatus used is illustrated in Fig. 2.

This apparatus, together with the sealed tube containing the ethane, and an ampule of degassed acetone, were placed within the Nitrogen Box. After the pressure had been reduced to below one micron, the box was filled with purified nitrogen. The ethane was then transferred to bulb A of the recrystallization apparatus and partly dissolved in about 30 ml. of acetone. The connecting tube was added, with the tap closed, and the apparatus was then removed from the Nitrogen Box and attached to the vacuum line. After the acetone had been cooled to -70° C., the box was evacuated and sealed off at C. The acetone solution was decanted into bulb B and part of the pure solvent was distilled back to bulb A by cooling this to 0 °C. This process was repeated until the greater part of the ethane had recrystallized in bulb B. Then the remaining acetone solution was decanted back to bulb A and the recrystallized solid was washed with a little of the pure solvent. Finally the acetone was cooled to -70°C. and the tube containing the recrystallized ethane was sealed off under vacuum.

Using the Nitrogen Box, this purified ethane was then transferred to a small vial within a specially constructed weighing-bottle. The design of the weighing-bottle gave some trouble, since it had to protect the ethane from atmospheric oxygen and yet be capable of evacuation within the Nitrogen Box. Eventually the type shown in Fig. 3a was employed. Just prior to the evacuation of the Nitrogen

FIG. 2

APPARATUS FOR RECRYSTALLIZATION OF ETHANE

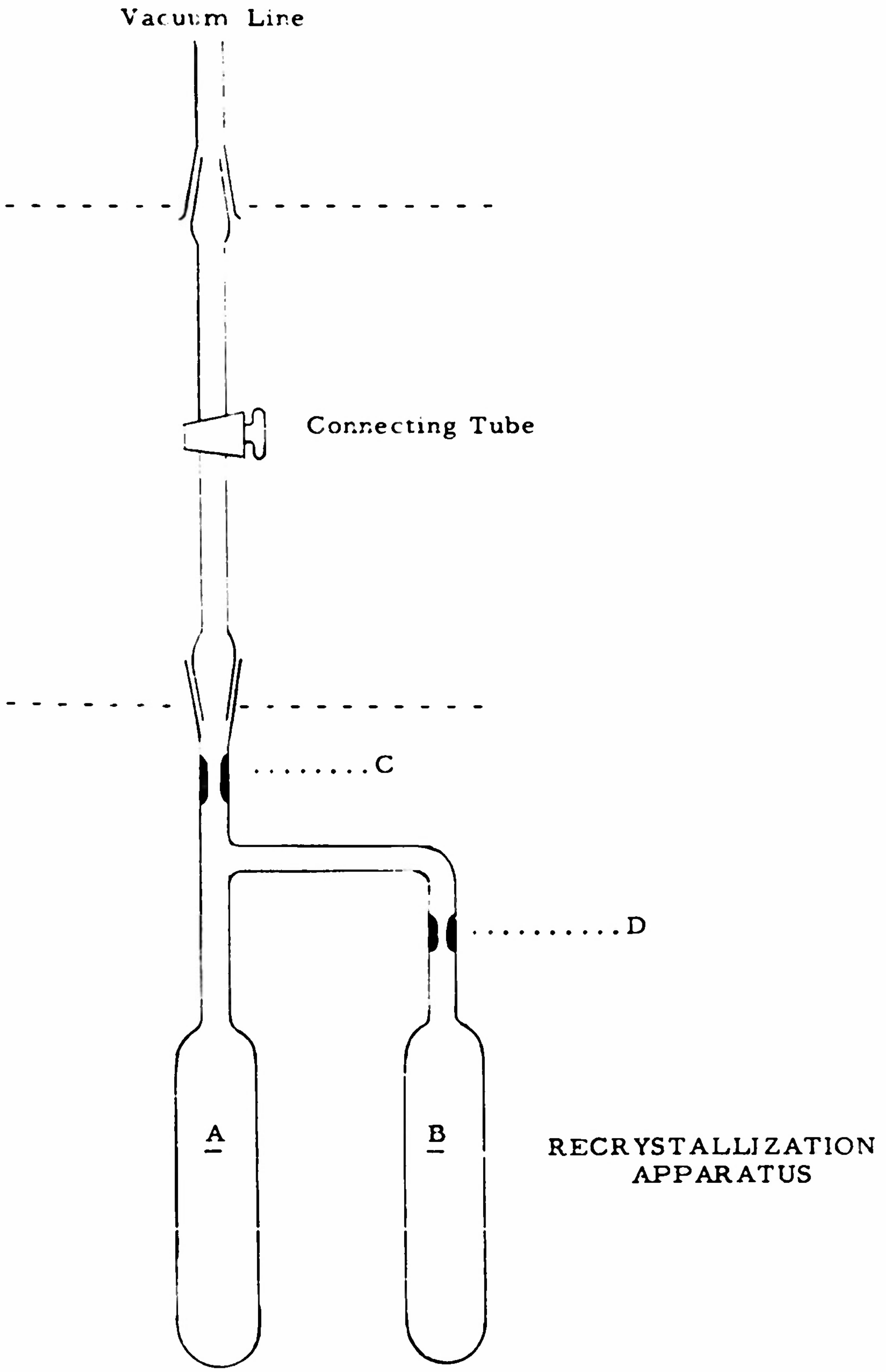
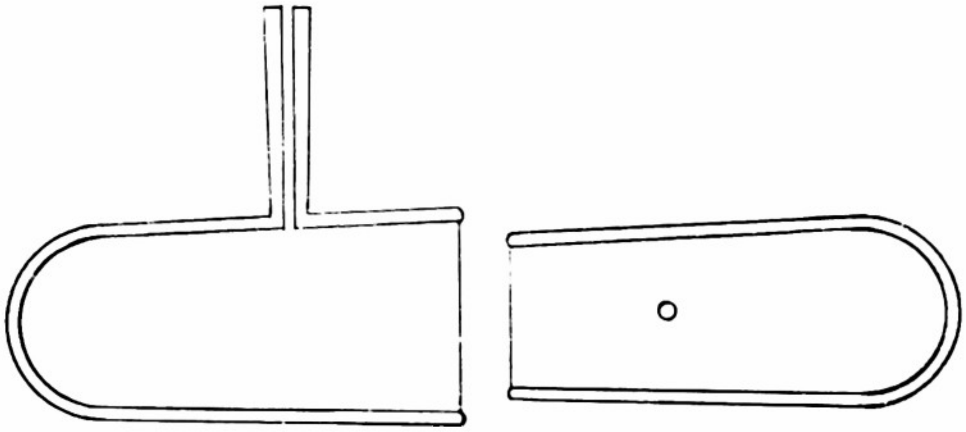
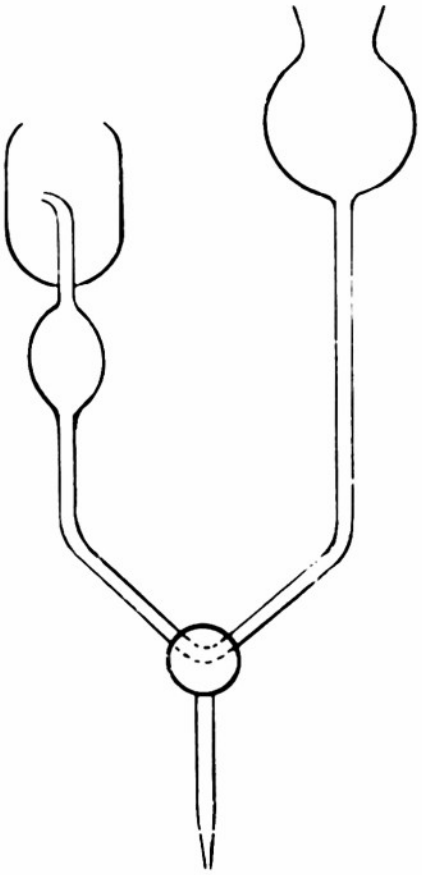

Vacuum Line
Connecting Tube
C
D
A
B
RECRYSTALLIZATION APPARATUS

FIG. 3a



THE WEIGHING BOTTLE USED TO CONTAIN THE VIAL OF ETHANE

FIG. 3b



AUTOMATIC PIPETTE FOR USE WITHIN NITROGEN BOX

Box, the two halves of the ground-glass joint were rotated so that the interior of the weighing-bottle communicated to the atmosphere through a length of capillary tubing. This allowed the bottle to be evacuated, while effectively preventing the interaction of oxygen with the ethane. Apiezon L grease was first used to seal the joint but this proved unsatisfactory in hot weather and Lubriseal grease was substituted.

When prepared in this way, hexaphenylethane forms almost colorless crystals, with a barely perceptible yellow tint. Providing oxygen is rigorously excluded* the ethane can be kept indefinitely in this form, but, in the presence of a trace of oxygen, the whole mass of ethane turns a uniform yellow color. However this appears to be mainly a surface reaction on the crystals, since, by a single recrystallization from acetone, the colorless ethane can be recovered in yields in excess of 50%. It is interesting that the yellow substance is soluble in acetone, indicating that little of the normal peroxide can be present.

Analysis of Hexaphenylethane

It is not easy to find a suitable analytical method for the estimation of hexaphenylethane. Many of the early workers estimated the purity of hexaphenylethane by measuring the volume of oxygen absorbed, calculating the ethane concentration from the equation:

$$Ph_3C \cdot CPh_3 + O_2 = Ph_3C \cdot O \cdot O \cdot CPh_3$$

However the normal peroxide can only be isolated in yields of 60% using oxygen, or 80% using air, even where the observed oxygen absorption corresponds to 100% reaction.[5] In a later section of this report, it is shown that triphenylmethyl peroxide is not the only product of the reaction of hexaphenylethane solutions with oxygen, an unstable yellow compound being also formed in quantities that are always small but very sensitive to the experimental conditions. Professor N. N. Lichtin of Boston University has recently stated (private communication) that the extent of oxygen absorption is also dependent on the experimental conditions, so this seems an unsuitable basis for an analytical method.

Ziegler[6] has studied the oxygen absorption of hexaphenylethane solutions in the presence of pyrogallol and has suggested that the product is then triphenylmethylhydroperoxide, this being formed by the transfer of a hydrogen atom from a pyrogallol molecule to a triphenylperoxy radical. This explains the greater oxygen absorption and fits the known behavior of pyrogallol as a radical inhibitor. However the hydroperoxide appears to undergo subsequent reactions, for none of it can be isolated from the solution. The hydroperoxide is known to be rather unstable, decomposing to yield phenol, benzophenone, and a little triphenylmethylperoxide.[7] It seems possible that these products,

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(5) Gomberg, Ber., 37, 3538 (1904).

(6) Ziegler, Ewald, and Seib, Ann., 504, 182 (1933).

(7) Wieland and Maier, Ber., 64, 1205 (1931).

together with the hydroperoxide, phenoxy radicals, and quinone derivatives formed from the pyrogallol, may cause further oxygen absorption, and this reduces the value of the method in analyzing for the ethane.

The reaction of hexaphenylethane solutions with benzoyl peroxide, has been reported by Hammond[8] as a possible method of analysis.

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[8] Hammond *et al.*, J. Am. Chem. Soc., 73, 3929 (1951); Hammond, Ravve and Modic, Anal. Chem., 24, 1373 (1952).

It is suggested that a trityl radical attacks a benzoyl peroxide molecule forming trityl benzoate and a benzoyloxy radical; the latter then either reacts with a further trityl radical or attacks the solvent. In benzene solution, the only products formed are trityl benzoate, benzoic acid, and tetraphenylmethane. Decarboxylation of the benzoyloxy radicals would be expected to interfere with this method, but Hammond's results show that, in benzene solution, this does not occur.

In our work, the purity of the hexaphenylethane has been estimated from its reaction with iodine. Gomberg[4] found that this reaction normally leads to an equilibrium concentration of triphenylmethyl iodide but Ziegler showed that the iodine uptake is quantitative if pyridine is added to the solution;[9] the product is then triphenylmethylpyridinium iodide. Ziegler

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[9] Ziegler *et al.*, Ann., 479, 277 (1930).

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was principally interested in following the reaction spectroscopically and added alcohol to the solution to prevent the precipitation of the compound above. The basic reactions are then as below:

$$Ph_3C\cdot + I = Ph_3C\cdot I$$

$$Ph_3C\cdot I + C_2H_5OH = Ph_3C\cdot O\cdot Et + HI$$

$$HI + C_5H_5N = C_5H_5NH^+ + I^-$$

but further side-reactions can lead to the formation of triphenylmethylpyridinium iodide and various periodides. This type of iodine-pyridine-ethanol solution in some neutral solvent was successfully used by Bachmann[10] in his experiments on the dissociation of pentaarylethanes but it was found that the formation of diarylmethylpyridinium iodides interfered with the subsequent back-titration of iodine with thiosulfate. Earlier work on this project[11] had shown that pyridine itself interferes with iodine-thiosulfate titrations by reducing the thiosulfate titer required. This effect can be prevented by the addition of acetic acid but the mechanism is unknown.

In the present work it was found that benzene solutions of iodine, pyridine, and ethanol, after the addition of hexaphenylethane, failed to give satisfactory endpoints when titrated with aqueous thiosulfate solutions.

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(10) Bachmann and Osborn, J. Org. Chem., 5, 29 (1940).

(11) Bartlett and Bender, Status Report to O.N.R., 14 September, 1949.

The reason for this was not determined but it was believed to be due to the formation of periodides by pyridinium hydroiodide and possibly by triphenylmethylpyridinium iodide. When the back-titration of iodine was carried out in a homogeneous medium, by the use of triphenylphosphine solutions, reproducible results were obtained. These solutions were made up in benzene containing 10% of 95% aqueous alcohol and 5% of pyridine. The following procedure was employed.

The preparation of the toluene solution of the hexaphenylethane, and its reaction with iodine, were carried out within the Nitrogen Box. The toluene and the iodine solution were degassed and introduced into the box as sealed ampules, the hexaphenylethane was stored under nitrogen in a small vial within the special weighing-bottle already described. After the Nitrogen Box had been evacuated and refilled with purified nitrogen, a small portion of the ethane, about 0.1 g., was transferred to a 25-ml. standard flask and dissolved in toluene. An automatic pipette, of the type shown in Fig. 3b, was then used to deliver samples of this solution into three conical flasks. This type of automatic pipette has no calibration marks but delivers a constant volume after it has been once washed through with the solution. Samples of the iodine solution containing 20% ethanol and 5% pyridine were run into these flasks from another automatic pipette and the flasks were then stoppered and left for an hour to allow the reaction to go to completion. The flasks were then removed from the Nitrogen Box and the excess iodine titrated against a benzene solution of triphenylphosphine or tri *p* chlorophenylphospine. The following reactions occur, the disappearance of the iodine color being a sufficient indication of the endpoint.

$$Ph_3P + I_2 = Ph_3P{\cdot}I_2$$

$$Ph_3P{\cdot}I_2 + H_2O = Ph_3P{\cdot}O + 2HI$$

$$2C_5H_5N + 2HI = 2C_5H_5\overset{+}{N}H + 2I^-$$

These titration values were compared with those obtained from further samples of the degassed iodine solution, delivered from the same automatic pipette. The difference in the titration values then gives the normality of the hexaphenylethane solutions in terms of that of the triphenylphosphine solution. Details of one of the analytical determinations are given in Table 1.

TABLE 1

Iodine Analysis of a Hexaphenylethane

Weight of Hexaphenylethane	0.1262 g.
Volume of Solution	25.8 ml.
Theoretical Normality of Ethane (as Radical)	0.0202 N
Volume of Automatic Pipette	3.54 ml.

	Volume of Tri-p-chlorophenylphosphine Soln.	
	Iodine Soln. after reaction with ethane	Iodine Soln. alone
Flask 1	4.05 ml.	(13.75 ml.)
" 2	4.04	13.25
" 3	4.00	13.27
Mean	4.03	13.26

Therefore 3.54 ml. ethane soln. $\approx$ 9.23 ml. phosphine soln.
Normality of phosphine solution (by iodine titration) 0.00646 N
Therefore ethane soln. 0.0168 N
Hence purity 83%

No special difficulty had been anticipated in the preparation of the pure ethane. However the results indicated that the crude ethane was 50-70% pure and the recrystallized ethane 80-90% pure. It should be mentioned that one batch of the ethane, estimated by thiosulfate titrations, came out to be 106% pure, but this value was not reproducible and only gave further reasons for doubting the value of iodine-thiosulfate titrations under these conditions.

These low values for the purity of the ethane were at first ascribed to the interference of oxygen during the reaction. This seemed possible since the early analyses were not carried out by the procedure above, but by injecting a degassed iodine solution through a rubber cap into a conical flask that contained the hexaphenylethane solution under nitrogen. However, when the reaction was carried out within the Nitrogen Box, the apparent purity did not increase.

It was then decided to accompany the hexaphenylethane analysis with a chloride analysis on the same solution. Samples of the toluene solution of the ethane (5 ml.) were evaporated to dryness and a dilute solution of sodium ethoxide in alcohol (5 ml.) was added. The alcohol was then evaporated off and the remainder was dissolved in water and filtered to remove the peroxide and other side products. The precipitate was thoroughly washed with distilled water and the combined filtrates were analyzed by the conventional Volhard proced e. The results of one of these analyses are given in Table 2.

These results, in conjunction with iodine analyses on the same sample, showed that only part of the low purity of the hexaphenylethane could be attributed to the presence of triphenylmethyl chloride. Thus iodine analyses on the sample used for Table 2 indicated that the ethane was 80% pure so the complete results for this sample are:

Hexaphenylethane	80%
Triphenylmethyl chloride	11%
Unknown	9%

TABLE 2

Volhard Analysis for Triphenylmethyl Chloride

Weight of Hexaphenylethane		0.1779 g.
Volume of solution		25.0 ml.
Theoretical Normality (as Radical)		0.0293 N.
	Flask 1	Flask 2
Volume of Silver Nitrate (0.0119 N)	5 ml.	5 ml.
Volume of Thiocyanate (0.0097 N)	4.65 ml.	4.69 ml.
Mean	4.67 ml.	
Normality of Chloride	0.00285	
Weight fraction (as $Ph_3C \cdot Cl$)	11%	

It was then considered that the hexaphenylethane might be forming an addition compound with a molecule of acetone. Gomberg had stated that this did not occur,[4] but his studies of other solvents show that the formation of an addition compound is sometimes determined by the temperature of crystallization; thus, in heptane solution,[12] such addition compounds are formed when the solvent is at room temperature, but not when it is hot. Gomberg's results do not suggest that the formation of these compounds is dependent on any structural group within the solvent molecules, and so presumably the difference between different solvents is quantitative, and all solvents may be expected to form such compounds providing the temperature of crystallization is sufficiently low. Examination for the presence of acetone molecules is particularly easy because of the strong infra-red absorption of the carbonyl group, and this was therefore used as the analytical technique.

Sufficient of the recrystallized ethane was dissolved in carbon tetrachloride to make a 0.1 M solution, assuming the ethane to be 100% pure. After the precipitation of the peroxide by oxygen, the filtered solution was examined in a Baird Infra-red Spectrophotometer; it showed only 3% absorption at 5.8 microns. A 0.1 M solution of acetone in carbon tetrachloride, under similar conditions, showed 88% absorption at this wavelength; it is evident that only a negligible quantity of acetone can be present in the ethane. However, the ethane solution showed characteristic absorption at other wavelengths, but, as a result of further evidence, this was attributed to the formation of side-products during the oxidation of the ethane. These reactions are discussed in another section of this report.

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(12) Gomberg and Schoepfle, J. Am. Chem. Soc., 37, 2569 (1915).

The main problem in this work seems to come from the failure of triphenylmethyl chloride to react completely with mercury. Possibly, mercury is an unsuitable choice, for Gomberg[13] reported the formation of a double salt of composition $2Ph_3C\cdot Cl\ \ 3HgCl_2$. However, molecular silver seems no better, for Selwood[14] showed that after shaking a solution of α-naphthyldiphenylmethyl chloride with a ten-fold excess of molecular silver for several hours, the reaction had not proceeded beyond 75% completion. In this work, it was decided to recrystallize the ethane once, and continue to a spectroscopic determination of the dissociation constant, using the iodine analysis as a guide to the purity.

Spectroscopic Studies

In this part of the report, the basis of the spectroscopic determination of the dissociation constant is discussed first, and then the experimental details and results. This part of the report is therefore divided into two sections.

(a) Theoretical Discussion

The spectroscopic determination of the dissociation constant is based on the difference between the absorption spectrum of hexaphenylethane and that of the triphenylmethyl radicals. The ethane

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(13) Gomberg, J. Am. Chem. Soc., 23, 496 (1901).

(14) Preckel and Selwood, J. Am. Chem. Soc., 63, 3397 (1941).

molecule would be expected to show the usual phenyl group absorption, but the triphenylmethyl radicals absorb light in the near ultra-violet and visible regions. This is an expected consequence of the greater conjugation in the radical structure. It is therefore possible to use the light absorption in these regions as a way of determining the radical concentration and thus of calculating the dissociation constant.

Determination of the radical concentration requires a knowledge of the extinction coefficient of the radical, but both this and the dissociation constant can be determined by a suitable plot of the experimental results. The relationship is derived below·

Let D........Optical density of solution
l........Cell length
a........Degree of dissociation
e........Extinction coefficient of the radical
S........Stoichiometric Conc. of ethane
K....... Dissociation Constant

Then $D = 2elaS = AaS$ ....Equation 1

and $K = \frac{4a^2S}{1-a}$ .... " 2

Substituting the expression for "a" from Equation 1, into Equation 2 and rearranging:

$$D = \frac{KA^2}{4} \cdot (S/_D) - \frac{KA}{4} \quad ....\quad (3)$$

Hence, if the optical density of a number of ethane solutions of different concentrations is plotted against the function $S/_D$, the slope is $KA^2/4$ and the intercept is $-KA/4$.

Therefore: $K = \frac{4(\text{intercept})^2}{(\text{slope})}$ ....(4)

and: $A = \frac{(\text{slope})}{(\text{intercept})}$ ....(5)

both the dissociation constant and the extinction coefficient can thus be found.

Although equation 3 was based on the assumption that the ethane was 100% pure, it can easily be corrected for the presence of non-absorbing impurities. These reduce the stoichiometric ethane concentration, so that if a plot of D against S/D is based on the apparent ethane concentration, as calculated from the weight of the crude ethane, the apparent dissociation constant will be too large, and must be multiplied by the fractional purity of the ethane. It is interesting that the presence of impurities has an opposite effect in the calculation of the dissociation constant from the magnetic susceptibility; then the radical concentration is directly measured and so the apparent dissociation is decreased when crude ethane is used.

Unfortunately, the presence of colored impurities distorts the relationship of equation 3 in a more complicated way. When their relative concentration is small, it is possible to allow for the extra absorption by adding a term "BS" in equation 1, so that:

$$D = AaS + BS \text{ ....(6)}$$

Substituting the expression for "a" from equation 6 into equation 2 then gives a new relationship between D and S/D.

$$4D = (KA^2 + KBA)(S/D) + 8BS - 4B^2S^2/D - KA \text{ ....(7)}$$

This shows that, as the ethane concentration is increased, the initial effect of colored impurities is to cause the graph of D against S/D to rise above the linear relationship expressed in equation 3, for D $>$ BS. Conversely, agreement with equation 3 is evidence for the absence of colored impurities.

The choice of a suitable wavelength for the measurement of the optical density requires a little care. The spectrum of three solutions of hexaphenylethane over the range 4000 A. - 5500 A. is recorded in Table 3 and plotted in Fig. 4. Now in determining the dissociation constant, it is necessary to work over the range of concentrations in which the degree of dissociation is rapidly changing; experiments at either end of this scale, by themselves, contribute little to the experimental result. From this point of view, the main maximum at about 5160 A. is most suitable, since it enables more dilute solutions to be used. However, experiments showed that this maximum is too sharp for accurate values of the density to be obtained, the apparent density depending on the slit width used. The experiments were therefore carried out on the relatively flat portion of the curve at 4200 A. Another possibility would be to use the very intense maximum reported by Anderson[15] at about 3350 A. but experiments indicated that this would restrict the results to excessively dilute solutions.

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[15] Anderson, J. Am. Chem. Soc., 57, 1673 (1935).

Experimental Procedure and Results

The preparation of the ethane solutions was carried out within the Nitrogen Box. The solutions were prepared in groups of three,

FIGURE 4

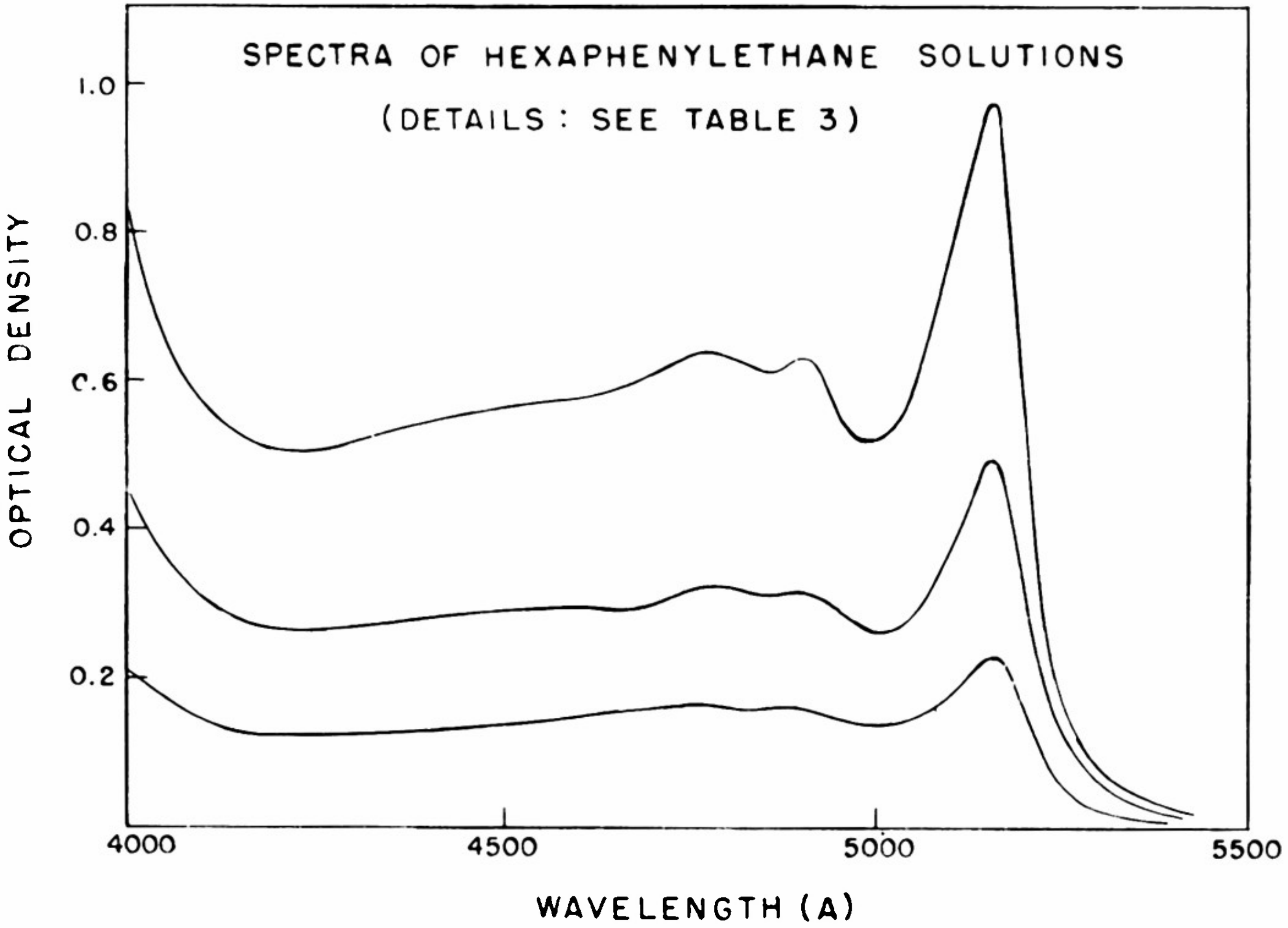
SPECTRA OF HEXAPHENYLETHANE SOLUTIONS
(DETAILS : SEE TABLE 3)
OPTICAL DENSITY
1.0
0.8
0.6
0.4
0.2
4000
4500
5000
5500
WAVELENGTH (A)

TABLE 3

Absorption Spectra of Hexaphenylethane Solutions

Solvent Toluene
Temp. 20°C.
Conc. Solution 1 0.00886 M.
Solution 2 0.00251 M
Solution 3 0.000712 M

	Optical Density (1 cm. cells)		
Wavelength (A.)	Solution 1	Solution 2	Solution 3
5500	0.030	0.013	0.007
5400	0.030	0.015	0.007
5300	0.078	0.043	0.021
5250	0.233	0.136	0.053
5200	0.670	0.362	0.170
5180	0.884	0.458	0.213
5160	0.960	0.491	0.232
5140	0.890	0.455	0.221
5120	0.812	0.406	0.202
5100	0.735	0.361	0.179
5050	0.578	0.283	0.143
5000	0.512	0.257	0.125
4950	0.555	0.283	0.140
4900	0.630	0.318	0.154
4850	0.605	0.307	0.156
4800	0.628	0.321	0.159
4750	0.628	0.321	0.161
4700	0.610	0.304	0.156
4600	0.570	0.290	0.145
4500	0.555	0.290	0.137
4400	0.538	0.283	0.130
4300	0.513	0.273	0.125
4200	0.501	0.265	0.121
4100	0.570	0.310	0.140
4000	0.840	0.450	0.201

Purity of Ethane = 80%

by dissolving some of the recrystallized ethane in degassed toluene and then performing two successive dilutions by means of an automatic pipet. The pipet was used to deliver a known volume of the original solution into a 25-ml. standard flask and then sufficient toluene was added to form a new standard solution. Samples of these solutions were transferred to 1-cm. Beckman cells, modified by the addition of a Pyrex joint and cap. The ground glass joint was lubricated with silicone grease, and protected the ethane solutions from oxygen when the cells were removed from the Nitrogen Box. Square Pyrex tubing was first used for the optical cells, but later Corex cells were substituted.

The optical densities were measured on a Beckman Spectrophotometer, modified as described by Noland[16] to allow accurate thermostating of the optical cells. The density was measured after the solutions had been thermostated for half an hour, and then again for a further hour. This second reading was to detect any diffusion of oxygen into the solutions or any decomposition of the radical solutions by light. The solutions listed in Table 3 are typical of the 20°C. runs, the mean deviation of the second reading being 0.003 density units. Unfortunately, this constancy is difficult to maintain when the thermostat temperature is increased to 40°C.

The stability of toluene solutions of hexaphenylethane was also investigated for longer periods of time. For solutions at room temperature and in the absence of light, the iodine analysis indicated 8% decomposition

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(16) W. Noland, Thesis, Harvard University, 1951.

in eighteen hours, and 20% decomposition in forty hours. Spectroscopic analysis, based on the absorption of the 5160 maximum, indicated 6% decomposition in twenty hours. This agreement may mean that some slow reaction always occurs in the solutions, but it is clearly too slow to interfere with the measurements of optical density.

TABLE 4

Optical Densities at 4200 A.

Solvent = Toluene Temp. 20°C. Cell length = 1 cm.

Batch No.	Solution No.	Conc. (M)	Density	S/D
A	1	0.00367	0.135	0.01165
A	2	0.000520	0.116	0.00448
B	1	0.00886	0.501	0.0177
B	2	0.00251	0.265	0.00948
B	3	0.000712	0.121	0.00588
C	1	0.0146	0.658	0.0222
C	2	0.00414	0.354	0.0177
C	3	0.00117	0.168	0.00697
D	1	0.00279	0.262	0.01065

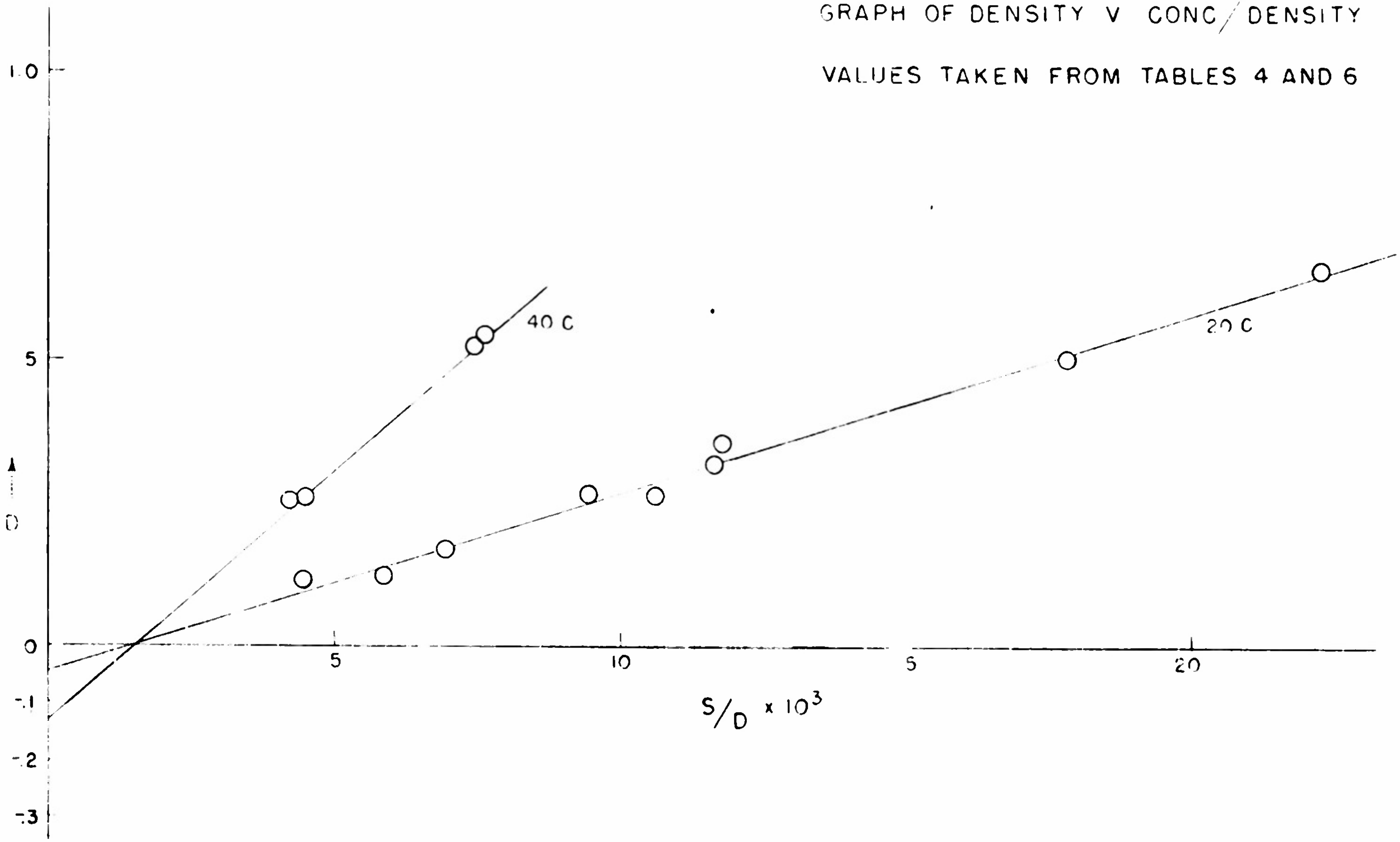
Purity of Ethane = 80%

The results for solutions thermostated at 20°C. are given in Table 4 and plotted in Fig. 5. An arbitrary limit of 0.100 was set on the optical density values, since, below this value, the percentage accuracy rapidly decreases. The best straight line was calculated on the principle of least squares and is drawn in Fig. 5; the calculated intercept is -0.0439 and the slope is 31.33. Substitution of these values in Equation 4 gives a dissociation constant of 2.5×10^{-4}, which, when corrected for the purity of the ethane, becomes 2.0×10^{-4}. This value is lower than that obtained by Ziegler[17] by a similar spectroscopic

FIG 5

GRAPH OF DENSITY V CONC/DENSITY

VALUES TAKEN FROM TABLES 4 AND 6



technique, but is in better agreement with the magnetic susceptibility measurements of Marvel,[18] Selwood,[14] and Muller.[19] The previous values are summarized in Table 5.

TABLE 5

Previous Values for the Dissociation Constant of Hexaphenylethane

Author	Method	Solvent	Temp.	K
Marvel	Magnetic Sus.	Benzene	20°C.	$1.8\ 10^{-4}$
Selwood	..	Toluene	20°C.	$1.7\ 10^{-4}$ *
Muller	..	Benzene	22-24°C.	$2.2\ 10^{-4}$
Ziegler	Optical	Benzene	20°C.	$4.1\ 10^{-4}$

*Calculated from other data given.

The experimental plot shows no marked curvature, and so does not suggest the presence of colored impurities. Nevertheless, the small value of the intercept on the density axis, coupled with the spread of the experimental points, indicates a considerable uncertainty in the final value of the dissociation constant. Equation 4 shows that the dissociation constant is proportional to the product of the intercepts

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(17) Ziegler and Ewald, Ann., 473, 163 (1929).

(18) Roy and Marvel, J. Am. Chem. Soc., 59, 2622 (1937).

(19) Muller and Muller-Rodloff, Ann., 521, 89 (1936).

on the two axes, so that, on this scale, the accuracy should be improved by increasing the slope of the plot, this can be done by raising the temperature or by using longer cells. The thermostating system could not be easily adapted for the use of longer cells, and so a series of measurements were taken with the solutions at 40°C.

Unfortunately, when thermostated at 40°C., the light absorption of many of the solutions showed a slow increase with time. The solutions were thermostated for about half an hour before the first readings were taken, and then a number of successive readings were taken at about ten minute intervals. The variation was believed to come from incomplete thermostating of the optical cells, for the glass tube leading to the Pyrex joint and cap projected above the thermostate bath and could cause condensation of toluene vapor. This may have led to a transference of grease from the cap of the cell to the radical solution, certainly the substitution of silicone grease for Lubriseal grease gave a marked improvement.

TABLE 6

Optical Densities at 4200 A.

Solvent Toluene Temp. 40°C. Cell length 1 cm.

Batch No.	Solution No.	Conc. (M)	Optical Density	S/D
B	1	0.00375	0.502	0.00747
B	2	0.00106	0.250	0.00424
C	1	0.00411	0.540	0.00761
C	2	0.00116	0.258	0.00449

Purity of Ethane = 88% *

*By difference (ϕ_3CCl anal'd, ethane used immediately; 8 days later when anal'd for $\phi_3C^{\cdot}$, purity down to 40%). It is assumed that this deterioration occurred after the optical measurements.

Nine solutions were measured at 40°C., and the densities of the four most stable solutions are given in Table 6 and plotted in Fig. 5. These did not change by more than 10% in the first hour. The graph leads to a dissociation constant of 7.9 10^{-4}, which, after correcting for the purity of the ethane, becomes 6.9 10^{-4}. From the results at 20°C. and 40°C., the heat of dissociation is 11,000 cal., in good agreement with the earlier work. Furthermore, Equation 5 shows that the intercept on the horizontal axis should be inversely proportional to the extinction coefficient of the radical, and the good agreement between the results at the two temperatures gives an internal check on the method.

Nevertheless, it must be admitted that this work is incomplete in its present state and requires further refinement. Much of the error probably resides in the density measurements and, since the graph passes below the origin, these have their greatest effect on the S/D values. However, a rigorous study of the dissociation of hexaphenylethane by this kind of approach seems to offer the best hope of obtaining an accurate value of the dissociation constant.

Discussion

Spectroscopic determinations of the dissociation constants of hexaarylethanes are of considerable theoretical interest, since, taken in conjunction with magnetic susceptibility measurements, they provide values for the diamagnetic susceptibility of triarylmethyl radicals. By themselves, the magnetic susceptibility measurements give only the average susceptibility of the hexaarylethane and triarylmethyl radicals. Previously, the diamagnetic susceptibility of the radicals has been assumed to be half that of the ethane, so that the diamganetism of the system is unchanged by dissociation. However, this has recently been questioned and two opposing suggestions have been made: the first by Selwood[20] assumes that an increase in diamagnetic susceptibility accompanies the increased resonance energy on dissociation; the second, by Pullman and Berthier,[21] assumes exactly the opposite. The evidence for these two hypotheses seems worth discussing in detail.

Selwood's suggestion is based on some experimental data and on the analogy with the increase in diamagnetism that accompanies resonance in cyclic aromatic hydrocarbons. Using the accepted values for the diamagnetism of the radicals, he showed that the magnetic susceptibility of the hexa p-biphenylethane solutions indicated an incomplete dissociation which was nevertheless temperature independent. This temperature effect strongly suggests complete dissociation and is supported by the work of Ting-Li Chu and Weissman,[22] who showed that solutions of the ethane obey Beer's Law on dilution. The simplest explanation for the anomalous magnetic results is that the assumed value for the diamagnetism of the radical is too low so that the calculated paramagnetism of the solution is too low also; this leads directly to a low value for the radical concentration. Owing to the anisotropy of the tri-p-biphenylmethyl radicals, the effective diamagnetism would be increased by any preferential orientation in the magnetic field, but this possibility is discounted by Selwood as a result of experiments on pyrene. There remains the possibility that a real increase in diamagnetism occurs during the dissociation of the ethane.

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[20] Selwood and Dobres, J. Am. Chem. Soc., 72, 3860 (1950).

[21] Pullman and Berthier, Compt. rend., 233, 1035 (1951).

[22] Ting-Li Chu and Weissman, J. Am. Chem. Soc., 73, 4462 (1941).

In spite of these experimental results, Pullman and Berthier[21] have suggested that the diamagnetic susceptibility of the two radicals is less than that of the ethane. These workers have developed the M.O. technique to allow the calculation of the anisotropic diamagnetism associated with the π electrons in a large number of conjugated systems.[23,24] In compounds such as benzene, it has long been

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(23) Mayot, Berthier, and Pullman, J. Phys. Rad., 12, 652 (1951).

(24) Berthier, Mayot, and Pullman, J. Phys. Rad., 12, 717 (1951).

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recognized that the diamagnetic susceptibility perpendicular to the benzene ring is far greater than that in the plane of the ring, and the difference (ΔK) between these values has been ascribed to the free rotation of the π electrons in molecular orbitals.[25] Pullman *et al.*

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(25) Lonsdale, Proc. Roy. Soc., A159, 149 (1937).

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express their results in terms of the ratio $\Delta K/\Delta K_{benzene}$, and, with the commonly studied aromatic hydrocarbons, their results agree with the earlier calculations of London[26] and with the experimental values. However, their results show that an increase in resonance energy, when based on the interaction of a benzene ring with an unsaturated side chain, can lead to a decrease in the diamagnetic contribution of the π electrons. In support of these calculations, they quote some of the extensive investigations of Pacault.[27,28,29]

When the same method is applied to the conjugation of the phenyl groups in triphenylmethyl radicals, the results indicate a value of 2.369 for $\Delta K/\Delta K_{benzene}$. Without conjugation of the benzene rings, this value would be 3 and so the resonance attending dissociation apparently reduces the diamagnetic susceptibility of the π electron by 1.262 K(benzene) for the two radicals. However, no mention is made of any correction for the partial inhibition of resonance due to the steric effect of the hydrogen atoms,[30,31] leading to a propeller-like structure for the radical. This, by reducing the interaction of

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(26) London, J. Chem. Phys., 5, 837 (1937).

(27) Pacault, Bull. Soc. Chim., 16, D371 (1949).

(28) Pascal and Pacault, Compt. rend., 219, 599 (1944).

(29) Pacault, Ann. Chim., 1, 527 (1946).

(30) Samilov and Dyotkina, Zhur. Fiz. Khim., 22, 1294 (1948).

(31) Dewar, Faraday Soc. Discuss., No. 2, 69 (1947).

the benzene rings, might cause the diamagnetic susceptibility to approach more nearly the classical value. Results are also given for other radicals, that for fluoryl showing a particularly large decrease in the anisotropic diamagnetism.

The effective decrease in the diamagnetism would be far less than the ΔK values, because of the constant contribution of the σ-bonded electrons. However, the significance of the effect lies not in its magnitude but in its direction. If this decrease is real, an alternative explanation is required for Selwood's anomalous results with tri-p-biphenylmethyl and, until this is given, other dissociation constants calculated from the magnetic susceptibility measurements seem rather suspect. The added significance thus given to the spectroscopic approach makes it the more regrettable that this investigation has not reached the accuracy required.

Appendix A Purification of Reagents

Triphenylmethyl Chloride

One hundred grams of Kodak "White Label" triphenyl-carbinol was recrystallized from carbon tetrachloride and 80 g. of the product was treated with 250 ml. benzene and 200 ml. conc. hydrochloric acid, following the procedure of Halford.[32] The mixture was shaken until the solid passed into solution. The hydrochloric acid layer was then removed and another 200 ml. of conc. hydrochloric acid added. After further shaking, the benzene layer was separated and stood for several hours over anhydrous calcium chloride. After filtration, about three-quarters of the benzene was distilled off and the remaining portion placed in a crystallization dish in a desiccator. The crystals of triphenylmethyl chloride, which separated on cooling, were washed with anhydrous ether and recrystallized from benzene (m.p. 112-113°C.). The product was stored in a desiccator.

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(32) Halford, J. Am. Chem. Soc., 53, 106 (1931).

Toluene

Merck "Reagent" toluene was shaken up with successive portions of conc. sulfuric acid until the acid layer remained colorless. The toluene was then washed with water and sodium bicarbonate solution, dried with calcium sulfate, and refluxed for several hours with sodium. It was then distilled and stored over calcium hydride in a reservoir on the vacuum line. Toluene, so treated, shows no cloudiness on cooling to -70°C.

Acetone

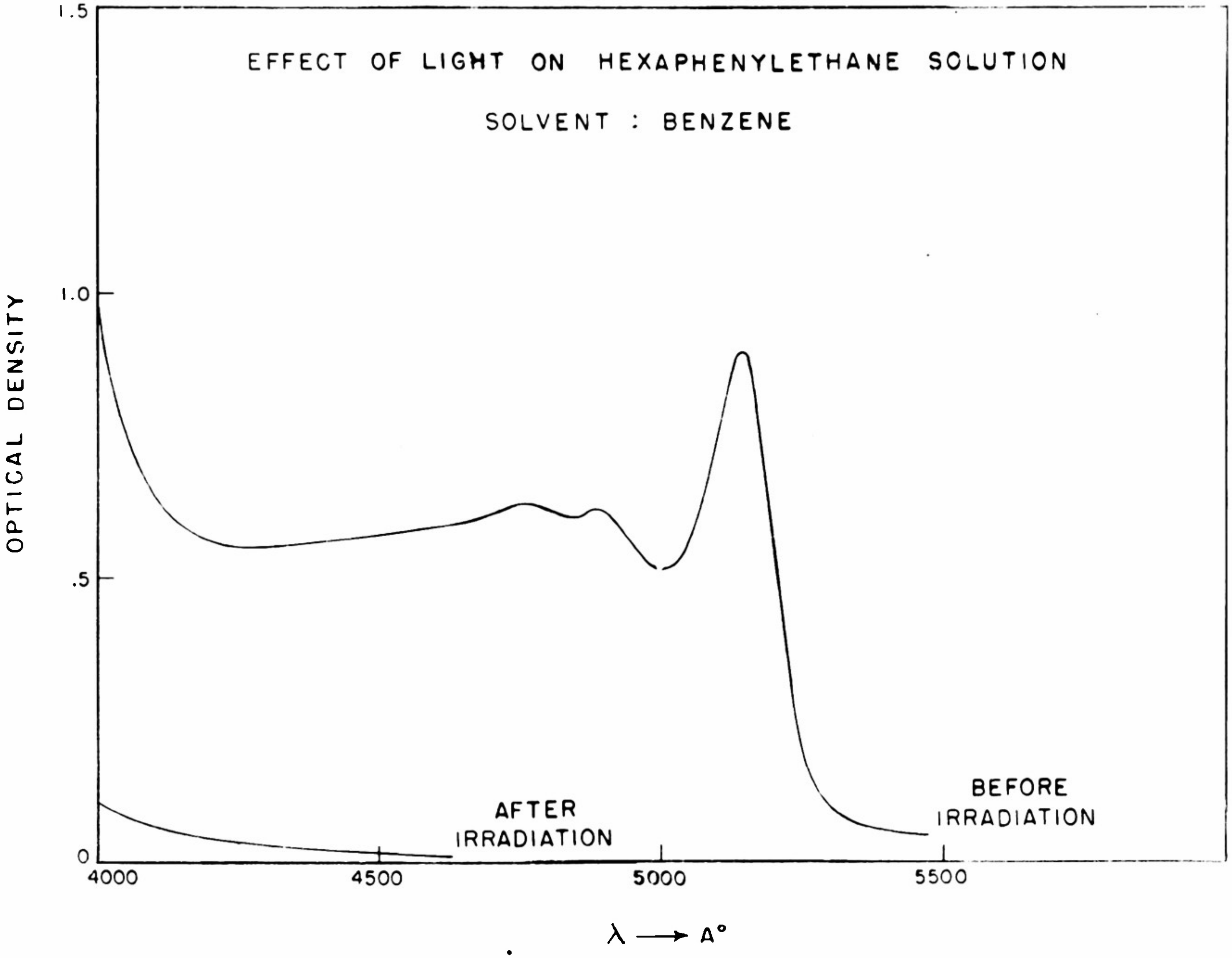
Mallinckrodt "Analytical Reagent" acetone was stored over calcium sulfate and distilled before use.

Appendix B The Reaction of Hexaphenylethane Solutions with Oxygen

In the course of this work it was observed that when solutions of hexaphenylethane were exposed to oxygen, the solutions did not become quite colorless but remained faintly yellow. At first, this was ascribed to the presence of a yellow impurity in the solid ethane. However, experiments showed that this was not true, and that the yellow compound was being produced in a side-reaction during the oxidation.

Two benzene solutions of hexaphenylethane of the same concentration were prepared from the same batch of solid material. One of these was allowed to react with oxygen, and then both were exposed for twenty hours at 30 cm. from a 100-watt tungsten lamp. The spectra of these two solutions, before and after exposure, are given in Figs. 6 and 7. The complete decolorization of the ethane solution, together with the stability of the yellow compound to light, shows clearly that the latter cannot be present as an impurity in the original solution. This was confirmed when subsequent experiments showed that the degree of yellow coloration was greater when oxygen was bubbled through the solution than when the solutions were shaken in air.

FIGURE 6



EFFECT OF LIGHT ON HEXAPHENYLETHANE SOLUTION

SOLVENT : BENZENE

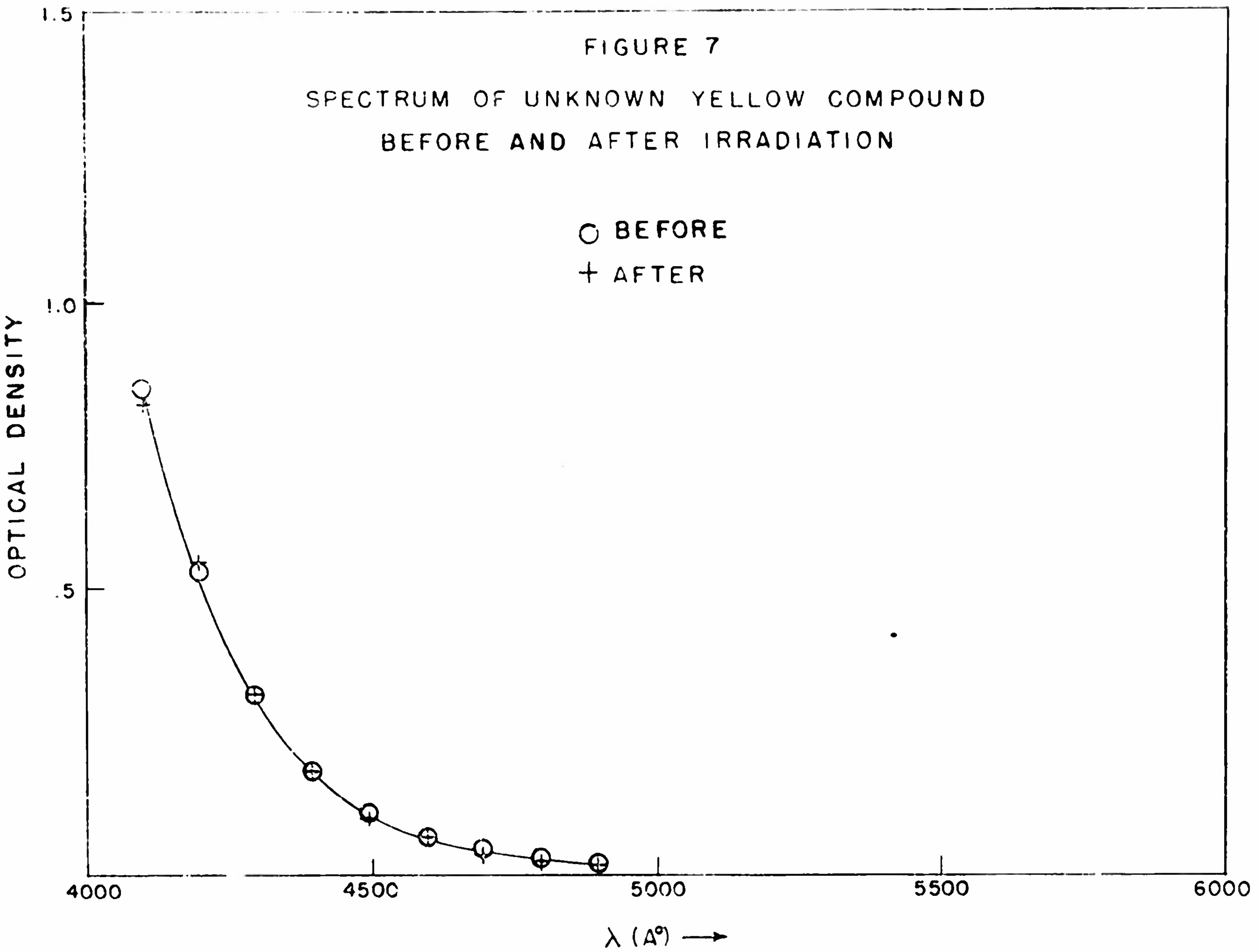


FIGURE 7

SPECTRUM OF UNKNOWN YELLOW COMPOUND
BEFORE AND AFTER IRRADIATION

When prepared from pure hexaphenylethane, the yellow solution is rapidly decolorized by a drop of concentrated hydrochloric acid, but, if the ethane has not been recrystallized, only partial decolorization occurs. This indicates that at least two yellow compounds are present, one being formed in a side reaction during the formation of the ethane. In spite of this complication, some experiments were carried out on the yellow solution obtained by allowing mercury to react with triphenylmethyl chloride in the presence of air. On filtration and evaporation, these solutions yield a yellow oil with a strongly phenolic smell. When an ethereal solution of this is shaken with aqueous potassium hydroxide, part passes into the aqueous layer, and acidification gives the basic fraction of the oil. The ether layer is faintly yellow and on evaporation yields a slightly yellow solid which rapidly liberates iodine from sodium iodie in glacial acetic acid. This was identified as triphenylmethyl chloride, part of the unreacted starting material.

The reaction of triphenylmethyl chloride with iodide ions was investigated using acetic anhydride as a solvent. The chloride liberates nearly twice as much iodine as would be expected from the equations below:

$$Ph_3CCl + I^- = Ph_3CI + Cl^-$$

$$Ph_3CI = Ph_3C^\cdot + I^\cdot$$

$$2Ph_3C^\cdot + O_2 = Ph_3CO.O.CPh_3$$

Presumably some hydroperoxide formation occurs. This problem was not studied further, since it had little bearing on the main dissociation measurements.

Appendix C Effect of Possible Diamagnetic Exaltation of Free Radicals on the Dissociation Constant of Hexaphenylethane as Determined by the Method of Magnetic Susceptibility

The Magnitude of Possible Diamagnetic Corrections in the Calculation of the Dissociation Constant of Hexaphenylethane

The magnetic method of determining the dissociation constant involves measurement of the apparent molar susceptibility of the ethane. This includes terms from the undissociated ethane and from the free radicals formed. Using the following nomenclature:

S = observed susceptibility

D = diamagnetic susceptibility of the ethane molecules

d = diamagnetic susceptibility of the free radicals
p = paramagnetic susceptibility of the free radicals
α = degree of dissociation

we have: $S = (1-\alpha)D + 2\alpha d + 2\alpha p$

or: $\alpha = S - D/2d - D + 2p$ . . . . [1]

Here, S is the experimental value D is -325×10^{-6} from Pascal's constants, p is 1260×10^{-6} at 20°C. and d is uncertain. The diamagnetic susceptibility of the free radicals is usually assumed to be half that of the ethane and on this assumption, the degree of dissociation α' is given by

$\alpha' = S - D/2p$ . . . . [2].

If this assumption is untrue the values of α' so calculated will be proportional to the correct values, for:

$\alpha/\alpha' = 2p/2d - D + 2p$ = constant.

However, the true and calculated dissociation constants are given by:

$$K = 4\alpha^2 C/1-\alpha \qquad K' = 4\alpha'^2 C/1-\alpha',$$

where C is the stoichiometric concentration of the ethane. K' will only be proportional to K as long as α is $\ll 1$; however, most magnetic measurements are carried out in this region.

Selwood[1] has suggested that the diamagnetism of the tri-p-biphenylmethyl radical is about twice the accepted value. It is worth seeing what difference this would make to the calculated dissociation constant of hexaphenylethane under typical conditions. Consider a 0.1 M solution of the ethane having a magnetic susceptibility of -275×10^{-6}. The "classical" dissociation constant is obtained by substituting in Equation 2 (at 20°C.)

$$\alpha' = -275 - (-325)/\ 2 \times 1260 \simeq .020 \ldots\ldots\ldots\ldots\ldots [3]$$

$$\therefore \quad K' = 4 \times (.02)^2 \times 0.1/.98 = 1.63 \times 10^{-4}.$$

Using Selwood's value for the diamagnetism d = D and

$$\alpha = -275 - (-325)/-325 + 2 \times 1260 \simeq .023$$

$$\therefore \quad K = 4 \times (.023)^2 \times .1/98 \simeq 2.15 \times 10^{-4}$$

Thus, if Selwood is correct, the present value for the dissociation constant of hexaphenylethane is too low by about 35%.

Pullman[2] has suggested that the accepted value for the diamagnetism of the radical is too high. He has calculated that the diamagnetic susceptibility of the π electrons decreases by about 20%, in dissociation of the ethane; however, no mention is made of any correction for the non-planarity of the radical. In benzene the π electrons are responsible for about 2/5 of the diamagnetic susceptibility and, to a first approximation, the same should be true of hexaphenylethane. Hence, if Pullman is correct, the diamagnetic susceptibility of the two radicals is not equal to that of the ethane but about 92% of this value, is about -299×10^{-6}. Substituting this value in Equation 2 gives

$$\alpha = -275 - (-325)/-299 - (-325) + 2 \times 1260 \approx .020.$$

Thus Pullman's calculation causes no significant change in the dissociation constants.

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(1) Selwood and Dobres, J. Am. Chem. Soc., 72, 3860 (1950).

(2) Pullman, Compt. rend., 223, 1035 (1951).